

## Urban Environmental Pollution 2013 – Creating Healthy, Livable Cities

## A novel recycling approach for transforming waste printed circuit boards into a material resource

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**Abstract**

The recovery of materials from urban waste has become progressively more important with wastes providing a variety of resources. This study focuses on the recycling of electronic printed circuit boards (PCBs) from mobile phones, computers, TVs, white goods, and micro-processors etc. that contain significant amounts of hazardous/toxic components along with a variety of metals, ceramics and polymers. Both formal and informal sectors are engaged worldwide in recycling such e-waste to recover precious and other metals (upto 40-70% of value). However poor recycling techniques, especially in developing countries, generate high levels of environmental pollution that affects both the ecosystems and the people living within or near the main recycling areas. Various e-waste recycling methods used in the informal sector include manual dismantling, open burning of PCBs, plastic chipping and melting, burning wires to recover copper, acid & cyanide salt leaching, and inadequate metallurgical treatments. These activities release dust particles loaded with heavy metals and flame retardants into the atmosphere that may re-deposit near the emission site, or be transported over long distances depending on their size. Significant levels of environmental pollution are thus associated with recycling e-waste.

This study presents an environmentally sustainable solution to e-waste management and reducing associated pollution during recycling. In this study, waste PCBs were heat treated in the temperature range 1150-1350°C for periods of up to 20 minutes in an Argon atmosphere. Key metallic constituents namely Cu, Sn and Pb showed a tendency to segregate out in the form of copper rich and Sn rich metallic balls. Minor elements such as Al, Fe, Mg, Ni, Pd, Pt and Zn segregated along with metallic droplets. Such high temperatures led to the removal of hazardous lead and the recovery of highly concentrated copper alloys and precious metals. Pyrolysis of PCBs also generated a carbon rich residue containing traces of Sn and very low levels of copper. Various ceramic impurities present precipitated out as slag and did not interfere with metal recovery.

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**Keywords:** Recycling; e-waste; recovery of materials; PCBs; environmental pollution.

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## 1. Introduction

Electronic waste, commonly termed ‘e-waste’ are end-of-life electric and electronic equipment considered obsolete by their users<sup>1, 2</sup>. Increasing consumption and short lifespan of electronic devices has become a waste management and urban pollution issue in recent years. The obsolescence of electronics has resulted in millions of tons of waste being discarded and landfilled. Between 20 to 50 million tonnes of e-waste are being generated each year worldwide<sup>3</sup>, increasing by 3 to 5% every year<sup>4</sup>. There are several difficulties with recycling e-waste. Various components of e-waste are a heterogeneous mixture of materials of varying composition, sizes and shapes; this complex waste is made up of metals, ceramics and plastics that may be valuable and/or hazardous in nature. There is no average composition of electronic wastes, as manufacturers are continuously changing components and applications<sup>5</sup>.

A number of valuable materials are also present in electronic waste. Copper and precious metals can amount from 40 to 70% of the total value in different types of e-wastes, making recycling attractive from an economical point of view<sup>5</sup>. For instance, one ton of waste mobile phones after battery removal contains up to 130 kg of copper, 3.5 kg of silver, 340 g of gold and 140 g of palladium that can be recycled and reused<sup>6</sup>. If all end-of-life mobile phones discarded in 2008 were recycled, 1250 ton Cu, 13 ton Ag, 3 ton Au and 2 ton Pd would be available for reuse, valued at US \$105 million<sup>7</sup>. Due to the wide range of electrical and electronic equipment available on the market, the European Union has divided e-waste types into ten categories (Table 1)<sup>8</sup>.

Table 1. E-waste categories<sup>8</sup>.

No.	Category	Label	Major electric and electronic equipment
1	Large household appliances	Large HH	Refrigerators, washing and cooking machines, electric fans, air conditioners.
2	Small household appliances	Small HH	Vacuum cleaners, irons, toasters, grinders, coffee machines, electric knives, hair-cutting, tooth brushes, clocks, watches, scales.
3	IT and telecommunications equipment	ICT	Mainframes, data processing, personal computers, laptops, notepads, calculators, printers, copying equipment, facsimile, telephones.
4	Consumer equipment	CE	Television and radio sets, video cameras, recorders, amplifiers.
5	Light equipment	Lighting	Luminaires for fluorescent lamps, straight or compact fluorescent lamps High-intensity discharge lamps, low-pressure sodium lamps.
6	Electrical and electronic tools	E&E tools	Drills, saws, sewing machines.
7	Toys, leisure, and sports equipment	Toys	Electric trains or car racing sets, video games, computers for biking, running, etc., coin slot machines.
8	Medical devices	Medical equipment	Radiotherapy, cardiology and dialysis equipment, pulmonary ventilators.
9	Monitoring and control instruments	M&C	Smoke detectors, heating regulators, thermostats.
10	Automatic dispensers	Dispensers	Automatic dispensers for hot or cold drinks, solid products, etc.

However, there are several issues and limitations associated with current practices of e-waste management and recycling. An informal sector has risen due to the opportunity for recovering valuable metals at low costs and has increased significantly in recent years due to the illegal exports of discarded electronics to developing and emerging economies. The informal sector generally uses poor recycling techniques, causing high levels of pollution and can cause severe damage to the environment and human health. Environmental pollution is caused by inappropriate recycling techniques by the release of hazardous components in e-waste after landfilling/treatment, agents, by-products and compounds in well-established recycling processes and by-products left after these processes.

This paper first presents an overview of the environmental pollution being caused by the current approaches being used to recycle e-waste. Key factors causing environmental damage have been identified. Details are then presented on a novel high temperature pyrolysis approach for recycling waste printed circuit boards (PCBs) that can be used to recover a wide variety of materials in an environmentally sustainable manner. This technique was used for producing various metallic and nonmetallic phases that could be used as material resource in a wide range of applications.

## 2. Environmental issues in e-waste management and recycling

A number of approaches are currently being used to manage e-waste around the world. In developing countries, most of the e-waste is mixed along with municipal solid waste and ends up in landfills and is generally not recycled<sup>9</sup>. Alternatively, several types of unsafe recycling processes are carried out to recover a small fraction of materials from e-waste, which can be detrimental to the health of people working and living around the recycling sites and to the environment<sup>10</sup>. Methods to recover materials from discarded products include manual disassembly, open burning to remove plastics and obtain the encased metals and acid digestion to recover precious metals<sup>11,12</sup>.

In transient economies such as China and India, e-waste management utilises more elaborate processes than those used in developing nations, e.g. in Africa. To recover metals from printed circuit boards they are heated/burnt with kerosene, propane and/or coal grills until the solder is melted. Chips are collected and can be sold or dissolved in acid to recover precious metals. Hydrometallurgical treatments are also used to recover metals; nitric acid has been used to recover gold, while hydrochloric acid is employed to extract copper. In both developing and emerging countries there is little awareness of the hazardous compounds being released during these practices<sup>13</sup>.

Transient economies also face another key issue that has caused significant concern; i.e. the illegal import and export of obsolete electronic equipment. A number of developed nations evade waste management regulations in their own countries exporting these residues under the cover of second hand devices. However, most of the exported goods are broken and not reusable converting developing nations thereby to a place for the disposal of end-of-life equipment<sup>11</sup>. Some of the countries that receive the exported e-waste are China (nearly a 70%), India, Pakistan, Nigeria, Indonesia, Philippines, among others<sup>14, 15</sup>. These economies are also facing a fast growth in e-waste from domestic consumption and subsequent generation of obsolete devices. The manufacturing processes also generate significant quantities of electronic residues and wastes<sup>10,16</sup>. The illegal imports as well as their own generation of e-waste have led to the development of an emerging informal sector to recover and recycle materials from e-waste, with providers taking benefit of low costs of recycling and cheap labour<sup>16</sup>.

In developed countries there are generally state-of-the-art facilities along with a well-established e-waste management protocol, consisting of a three-step recycling approach. Collection is the first step of the recycling chain and a key stage, as this identifies the amount of e-waste available for the recovery of materials. Disassembly and pre-processing includes sorting, dismantling and mechanical processes to separate hazardous materials and valuable components. These separation processes may be skipped for small and complex e-wastes. End-processing involves metallurgical treatments such as pyro and hydrometallurgy to upgrade the content of valuable materials to subsequently recover them, including refining processes and disposal of by-products and wastes. Every step of the recycling chain has to be managed efficiently to enhance productivity and minimising losses<sup>6, 13</sup>.

A broad range of hazardous and toxic components are associated with different types of e-waste; these can be classified into three types, namely, primary, secondary and tertiary. Primary components involve hazardous elements contained in e-waste. Secondary products are by-products or residues generated after an inappropriate recycling process, while tertiary emissions are compounds used during recycling that could cause severe environmental and health issues when handled unsafely<sup>6</sup>.

### 2.1 Primary contaminants

Primary components are present in several types of e-waste. High levels of heavy metals such as lead, mercury, nickel and cadmium are present in batteries<sup>12</sup>. Cathode ray tubes (CRT) contain Ba, rare earth elements as well as ~2 kg of lead in monitors<sup>12, 15, 17</sup>. Lead present in various e-waste can leach out to the ground if the glass is crushed<sup>18, 19</sup>. Lead is also found in fluorescent tubes<sup>17</sup>. The impact of lead could be catastrophic on the human body, as it may affect the central, hematopoietic, genitourinary and reproductive systems<sup>20</sup>.

Varying plastics present in e-wastes can contain >100 mg/kg cadmium, and more than 1000 mg/kg of Pb, Sn, Ni, Sb and Zn, that get released upon combustion or dissolution<sup>21</sup>. Toners and cartridges also contain cadmium as well as other hazardous and toxic chemicals<sup>4</sup>. Some common components of printed circuit boards (PCBs) are Pb from tin-lead solders<sup>17</sup>, Cd used in solder, chip resistors, infrared detectors and semiconductors<sup>4</sup>, Sb, Zn and Cr<sup>14</sup>. Cadmium may accumulate in the kidneys and can cause cancer<sup>22</sup>.

Nearly 12% of the plastics used in electric and electronic devices contain flame retardants, e.g. TVs and computers<sup>5, 12</sup>, which can be found in the form of hazardous solids such as polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs) and tetrabromobisphenol-A (TBBPA)<sup>12</sup>. PBDEs and TBBPA may accumulate in

the soils and consequently leachate from landfills, as there are no bonds between them and plastics<sup>23</sup>. Exposure to PBDE may affect levels of thyroid hormones and cause genotoxic damage<sup>24,25</sup>. TBBPA is known to be an endocrine disruptor, specifically disruption of thyroid homeostasis. Since the early 1970s PBBs are no longer produced and used, however may be present in e-waste from first generation devices<sup>26</sup>.

Liquid crystal displays also known as LCDs contain lead, mercury, indium, tin and zinc. Mercury is also found in fluorescent lamps, switches, thermostats, sensors, among others<sup>4, 12</sup>. Mercury can leach out or vaporize from landfills<sup>27</sup>. The effects of Hg on health are irreversible, as it can damage the central, genitourinary and peripheral nervous systems, foetus and it may bio-accumulate, especially in fish, entering into the food chain<sup>20,28</sup>.

Capacitors, condensers and transformers use polychlorinated biphenyl (PCB) among its components, which increases the risk of cancer in humans due to oxidative stress<sup>4, 12, 19, 29</sup>. Fridges, air conditioners and freezers contain chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFC) or hydrofluorocarbons (HFCs), which are present in the insulation foam and if landfilled these gases may get released from the appliances<sup>4, 30</sup>. These gases act as greenhouse gases, therefore damage the ozone layer and contributing to global warming and climate change<sup>31</sup>.

Other elements present in e-wastes are americium, chromium, gallium, selenium and beryllium, that are found in smoke detectors, data tapes, semiconductors and rectifiers, respectively<sup>12</sup>. Effects of chromium on health have been extensively studied; inhalation and/or ingestion of toxic hexavalent chromium compounds may cause allergy, ulcers, gastroenteritis, renal and hepatocellular deficiency and lung cancer<sup>32</sup>.

## 2.2 Secondary contaminants

Secondary hazardous components are generated after inappropriate recycling processes, and include various hazardous elements and components. During hydrometallurgical processes, volatile compounds of chlorine and nitrogen can be released, as well as spent acids and sludges are left after the process<sup>13</sup>. The spent acids generated after leaching contain heavy metals, PBDEs, PCBs and polycyclic aromatic hydrocarbons (PAHs)<sup>33</sup> which are disposed into the water or soil<sup>34</sup>, while other rejected parts are disposed of on the recycling site and may contain heavy metals as well; these contaminate the immediate area surrounding the recycling facility area<sup>11</sup>.

The incineration of plastics containing flame retardants can produce toxic components, such as PAHs and polyhalogenated aromatic hydrocarbons (PHAHs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs and PCDFs)<sup>4, 12</sup>, and polybrominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs)<sup>35</sup>. Insulated copper wires are also burned openly can generate 100 times more dioxins than burning domestic waste<sup>36</sup>. These pollutants are dispersed through the air and can be found in air, dust and water around recycling sites, causing severe environment issues and reaching food chains<sup>12, 37, 38</sup>.

PAHs can cause lung, skin and bladder diseases and may cause cancer over extended exposure<sup>22</sup>. Exposure to PCDD/Fs can cause gastrointestinal, hepatic, dermal and neurologic toxicity issues in human health, and reproductive and immunologic toxicity in animals<sup>39</sup>. Animal exposure to PBDD/F can cause reproductive issues, immunotoxicity and lethality, among others<sup>40</sup>. In general, the exposure to dioxins can affect breast milk, placenta and hair, which may cause cancer and other health issues<sup>41</sup>.

Metals and other hazardous substances have been measured in air, soil, freshwater and rivers around PCB workshops in Guiyu, China; Cr, Zn, Pb, Mn and Cu content in air samples were found to be much higher than any other site in Asia. PAH were also analysed and were 2-6 times higher than expected levels, while PBDE concentrations were found to be 58-691 times higher<sup>24, 42</sup>. PCDDs/Fs and PBDDs/Fs were analysed by Li et al.<sup>43</sup>. The concentration of PCDDs/Fs in air was found to be the highest ever documented in the world; the concentration of PBDDs/Fs were also very high. Contaminants were found in dust samples from PCB workshops exposing workers to high concentrations of Sn, Pb, Cd, Cu, Ni, Ag and Zn<sup>34, 37</sup>.

Analyses of hazardous elements in soils have shown a high level of contamination in urban areas near PCB workshops. Cu and Pb were found to be 155 and 371 times higher than other sites<sup>34</sup>, while PBDEs, PCDDs/Fs, and PAHs were also found high. These levels are associated with leaching and open burning activities<sup>33, 44</sup>.

In rivers Lianjiang and Nanyang in Guiyu, China, Wong et al.<sup>45</sup> found high levels of As, Cr, Li, Mo, Sb and Se in Lianjiang, while in Nanyang elevated levels of Ag, Be, Cd, Co, Cu, Ni, Pb and Zn were measured; both were attributed to leaching associated with the recycling of printed circuit boards near the rivers. The sediments of the rivers also had high levels of Cd, Cu, Ni, Pb and Zn<sup>46</sup>.

Hazardous elements spreading through water, soils and air have severe consequences on people's health. Issues such as skin, stomach and breath ailments and high levels of lead and copper have been observed in workers and residents, especially children. Elevated levels of chromium in umbilical cords and even leukaemia cases have been recorded<sup>47-50</sup>.

Several problems are associated with different stages of the recycling chain. In the disassembly process there are issues related with the handling of hazardous substances such as mercury found in fluorescent tubes or switches<sup>51</sup>, or CRTs containing lead<sup>13</sup>. In the pre-processing step, shredding process can generate dusts composed of metals, plastics, ceramics and silica, which could either be inhaled or may come in contact with skin of the workers. The dusts can also contaminate the environment. Hazardous components are also released during shredding, such as cadmium and lead<sup>52</sup>, as well as PBDEs, TBBPA and hexabromocyclododecane (HBCD) and PBDDs/Fs from plastics containing brominated flame retardants<sup>53, 54</sup>. HBCD are bio-accumulative and persist in the environment. These can affect thyroid hormone levels and may cause increase learning, memory and behaviour defects in newborns<sup>26</sup>.

### 2.3 *Tertiary contaminants*

Tertiary emissions may occur during pyro-metallurgical processes, such as the release of Cu, Pb, As, Cd and Cr in the gas fraction<sup>55, 56</sup>. Special concerns have been raised about the high temperature processes for recycling e-waste due to PCDDs/Fs, PBDDs/Fs and mixed chlorinated-brominated dibenzodioxins and furans (PXDDs/Fs) could be emitted<sup>57</sup>. Investigations have found that if an appropriate treatment of off-gases is carried out, these compounds could decompose or be isolated<sup>58, 59</sup>. Greenhouse gases such as CO and CO<sub>2</sub> are also emitted during pyro-metallurgical steps. The use of fluxes and salts as well as the inherent generation of slags during treatment may also have an environmental impact as these may retain quantities of heavy metals and other hazardous elements, such as Pb, Cd, Cr, As, Sb, Bi, among others.

Hydrometallurgical processes also have several issues, especially related to high amounts of secondary wastes generated during the treatment. Current processes employ high quantities of sulphuric acid in leaching and solvent extraction steps to recover mainly copper and precious metals present in e-waste. The spent acids left after the process cause serious environmental and health issues, due to the leaching and evaporation of substances into the water, soil and air, reaching the food chain and people directly<sup>13, 60</sup>. In solvent extraction processes, dense organic liquids are employed, these are disposed of after their useful lifespan, causing environmental issues as well. In the case of printed circuit boards, the agents may not reach the internal layers of boards, the leaching of PCBs with aqua regia or nitric acid can generate nitrogen oxide vapours and chlorine vapours, so the gas release needs to be efficiently controlled<sup>6</sup>.

Several studies have been carried out to recover metals from e-waste using hydrometallurgical techniques. Most of them have employed nitric acid, aqua regia, cyanide, hydrochloric acid and other chloride solutions, thiourea and bromide in leaching and concentrations steps. These liquid residues are disposed of after treatment; no reutilisation has been found. Regarding solid secondary wastes, sludges may contain heavy metals, as the precipitation of mercury and lead have been observed. Other solids containing plastics and other metals and also activated carbon are left behind after concentration processes. These solid and liquid residues may cause severe environmental issues and release of metals and other elements may occur, affecting people and fauna in several ways<sup>61-64</sup>.

Inappropriate e-waste treatment can cause severe and irreversible damage to the environment, fauna and human health, as a wide range of pollutants may be released or generated during several types of formal and informal recycling processes. E-waste are a worldwide problem and greener solutions need to be found towards a sustainable management of discarded electronics, recovery of materials, reduction of waste volumes landfilled and minimisation of environmental pollution.

### 2.4 *Limitations of current approaches*

Several limitations of current recycling approaches have been observed, mainly due to secondary wastes and emissions occurring during recovery processes. Issues with mechanical pre-processing techniques have been identified, such as handling hazardous substances in disassembly step; dusts generated in shredding process containing PBDE, TBBPA, PBDD/Fs and heavy metals, among others. Mechanical processes also contribute to the loss of precious metals.



Hydrometallurgical recycling processes have several limitations and disadvantages, especially due to the secondary wastes generated such as spent solutions used in leaching steps; sludges containing heavy metals, PBDEs, PCBs and PAHs, and organic liquids from solvent extraction. Other solids are also left behind after processing, such as polymers, metals and carbons. These residual by-products are disposed of in water and/or soils, which can leach out or evaporate hazardous substances. Volatile and toxic compounds can also get released during hydrometallurgical processes, such as nitrogen oxide vapours and chlorine vapours.

In pyrometallurgical approaches, several pollutants could be emitted such as PAHs, PHAHs, PCDD/Fs, PBDD/Fs generated from the incineration of flame retardants present in plastics. Metals can also get released in the gas fraction, greenhouse gas emissions that can be even higher if gas/oxygen is used in the process, which also result in the loss of carbon within the gas phase. Open burning and pyrometallurgical techniques also generate by-products which are disposed of on the ground or landfills.

Other limitations are the temperatures commonly used to incinerate/pyrolyse electronic wastes are not adequate for recovery aims and minimisation of pollution. Also, the focus of investigations and current recycling approaches are on the recovery of only one material/metal, so many secondary residues are left after processing. Most of these limitations can be addressed by optimising the process conditions and establishing an appropriate use of by-products obtained after processes.

### 3. Aim of the study

The aim of this research was to investigate the recovery of metallic and non-metallic phases from waste printed circuit boards in an environmentally friendly way. High temperature pyrolysis was carried out at temperatures above the melting point of copper in order to avoid dioxin formation and to probe simultaneous extraction of other metals along with molten copper. Heat treatments were performed under inert atmosphere, avoiding re-oxidation of metals, maximising their recovery as well as reducing the greenhouse gas emissions; retaining carbons in the residue during recycling. The generated products could be used as a resource of materials.

### 4. Experimental

A mixture of several types of computer waste printed circuit boards (PCBs) was processed through a high temperature pyrolysis to recover a range of materials. Specimens were heat treated at the temperatures of 1150°C, 1250°C and 1350°C and the samples comprised PCBs of different natures (polymer-rich, silica-rich, among others), which were provided by Steinert (Melbourne, Australia). In this investigation, PCBs were manually crushed to a size of ~1cm<sup>2</sup> and random pieces were used – the results are therefore quite general as no specific type of PCBs was studied. Several pieces weighing a total of 1 g were placed into an alumina crucible and put into the cold zone of a high temperature horizontal tube furnace, which had a length of 1 m, internal diameter 5 cm and wall thickness 5 mm. The reaction assembly was held there for five minutes at temperatures in the range of 250°C – 350°C to avoid thermal shock, and then pushed into the hot zone of the furnace for 10 and 20 minutes. High purity Argon was passed continuously through the furnace at a rate of 1 L/min. the gas outlet was connected to an Infrared Analyser for monitoring of CO, CO<sub>2</sub> and CH<sub>4</sub> produced during the heat treatment. Samples were pulled back to the cold zone for another five minutes to avoid thermal cracking and the re-oxidation of the products. Five experiments were carried out at each temperature to enhance the reproducibility of results. Solid products were observed to be in the form of metallic droplets and a carbonaceous phase. The metallic phase was analysed using Scanning Electron Microscope (SEM) – Energy Dispersive Spectroscopy (EDS) model Hitachi S3400X and Inductively Coupled Plasma Optical Emission Spectrometers model Perkin Elmer Optima 7300DV ICP-OES techniques. The carbonaceous residue was also analysed through ICP-OES; the chemical composition of metals distributed within both metallic and non-metallic phases was investigated. More details can be found in Cayumil et al.<sup>65</sup>

### 5. Results

A gaseous fraction mainly composed of CO, CO<sub>2</sub>, CH<sub>4</sub>, a metallic phase and a carbonaceous/slag residue were produced during heat treatment of waste PCBs in temperature range 1150°C-1350°C. Detailed ICP-OES and SEM-EDS results on solid residues were obtained. Metallic phase was one of the key components of residual solids and was composed of red and white droplets that segregated out naturally after the heat treatment. A carbonaceous/slag residue was also obtained, labeled here as non-metallic fraction (NMF). Both of these components could be easily separated upon cooling. ICP-OES analyses of the balls and carbonaceous residue found these to be predominantly

metallic and carbon & refractories respectively. Metallic elements were further classified into major and minor components, with minor being categorised into three groups: base metals, precious metals and slag-forming metals. Quantitative results of these elements distributed into the metallic and non-metallic fractions are given below. The measurement method itself is highly accurate ( $\pm 0.1\%$ ), however, the deviation could be as high as  $\pm 5\%$  due to the composition of each sample being variable. Analysis reported is representative of various samples used in the present experimental investigation.

### 5.1 Distribution of major elements

Main metals found in the droplets obtained in the range of temperatures were copper, tin and lead. ICP-OES and SEM-EDS analyses showed that red droplets were mainly composed of copper, while the white droplets were composed predominantly of tin with small amounts of lead. Relative distribution and proportion of these metals in various solid fractions obtained at 1150°C, 1250°C and 1350°C after 10 minutes of heat treatment is shown in the Fig. 1. These results are presented as wt. % due to quite high concentrations of major metals in various droplets.

ICP-OES analysis of copper-rich balls showed that tin and lead were also distributed within these droplets, but in significantly lower quantities as compared to copper. The analysis of tin-rich droplets showed higher amounts of lead compared to copper-rich droplets and also lower quantities of copper. Quantities of lead in the residue were much lower than in the metallic phase. Lead amounts were seen to decrease with increasing temperature. Copper concentrations in tin-rich white droplets were also found to increase with temperature. It can be seen that the highest amount of copper in the metallic phase was observed in red droplets at 1150°C and was found to decrease somewhat at higher temperatures.

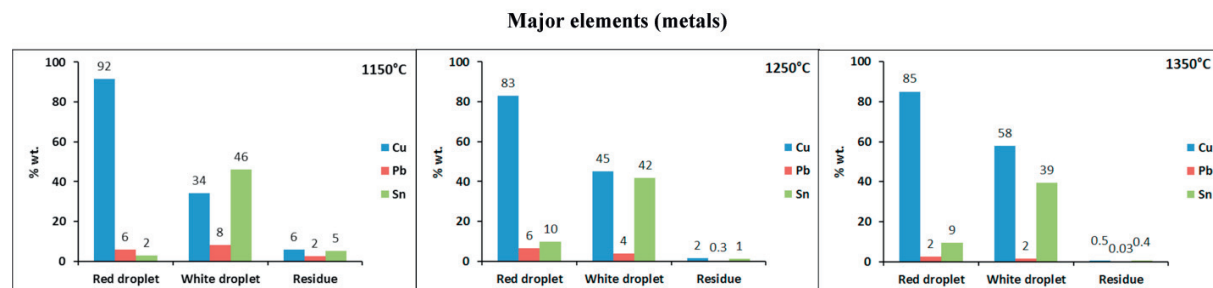


Fig. 1. Distribution of copper, tin and lead within three solid fractions.

### 5.2 Distribution of minor elements

Metals found in minor quantities within the solid fractions were classified into three groups: base metals, precious metals and slag-forming metals, with amounts typically found in ppm quantities. Their distribution in copper-rich droplets, tin-rich droplets and NMFs obtained in range of temperatures studied and 10 minutes of heat treatment is presented in this section. Nickel, iron and zinc were found in the metallic phase and the carbonaceous/slag residue as well. Metals distribution at these working temperatures is shown in Fig. 2. It could be observed from the results that iron tended to remain in the NMFs to a greater extent, while Ni and Zn were found spread predominantly within the droplets. This behaviour was observed at all three temperatures.

Silver, gold, palladium and platinum were also observed in the ICP-OES analysis of the three solid fractions. The distribution of these elements is shown in Fig. 3. Gold was usually found as a trace element and was generally below the detection limit. These metals tended to remain in the metallic phase either within the copper-rich and tin-rich droplets and were seen in much lower amounts in the NMFs at these temperatures, showing a tendency to be linked with the major elements recovered after processing. Aluminum and magnesium, which are main components of ceramics from raw PCBs, were found distributed in greater amounts within the NMFs at these temperatures. Trace quantities were also found within copper-rich and tin-rich droplets (Fig. 4). This behaviour was observed in all heat treatments – no significant differences were observed with changing temperatures.

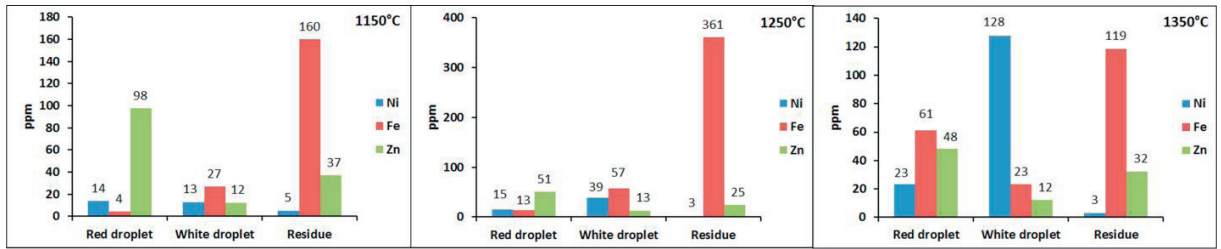
**Minor elements (base metals)**

Fig. 2. Distribution of nickel, iron and zinc within three solid fractions.

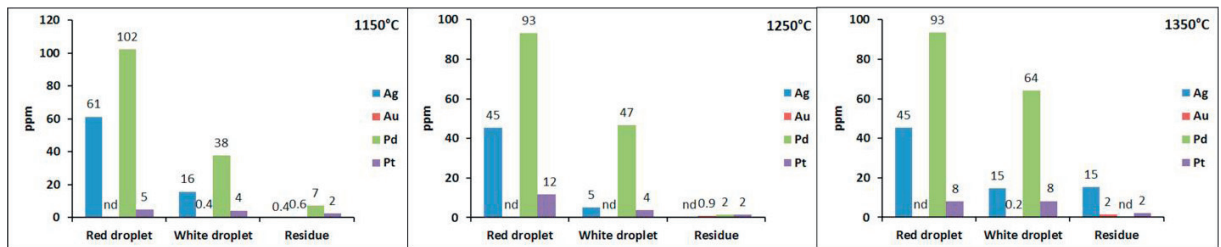
**Minor elements (precious metals)**

Fig. 3. Distribution of silver, gold, palladium and platinum within three solid fractions.

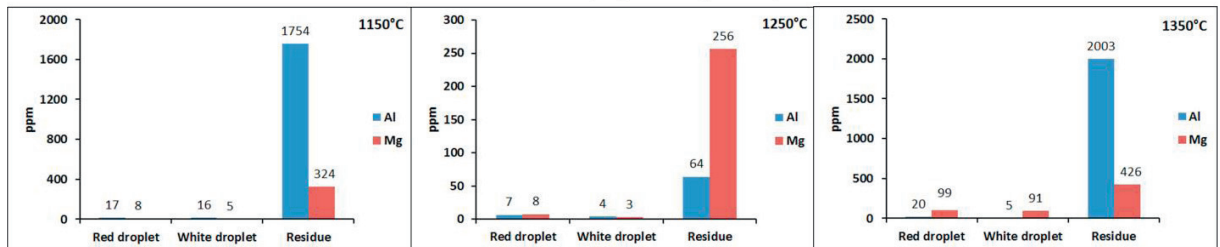
**Minor elements (slag-forming metals)**

Fig. 4. Distribution of aluminum and magnesium within the solid fractions obtained after heat treatments at 1150°C, 1250°C and 1350°C.



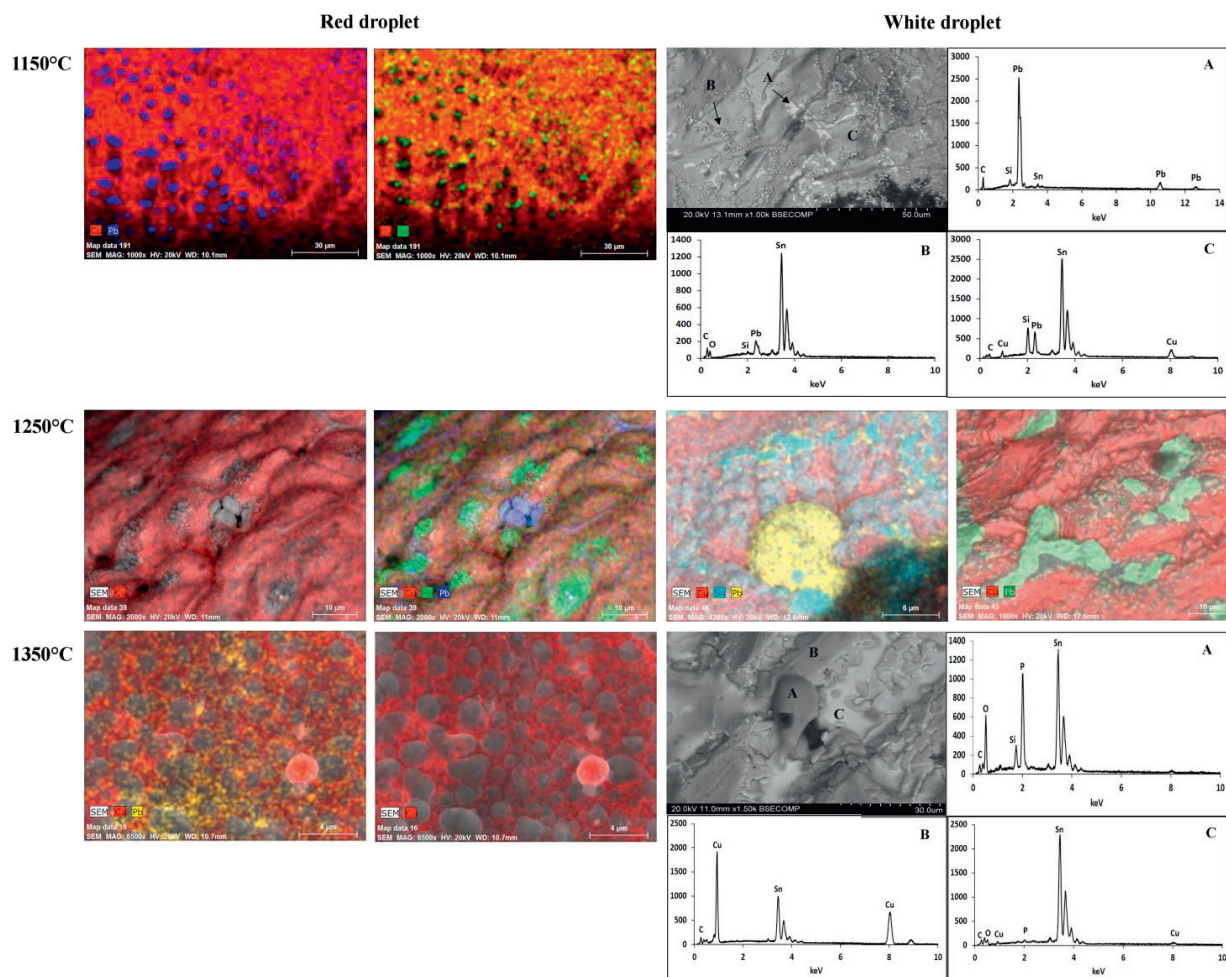


Fig. 5. SEM-EDS images of copper-rich and tin-rich droplets obtained after heat treatments at a range of temperatures.

### 5.3 SEM analysis of residual solids

Metallic droplets obtained after 10 minutes of heat treatment at all temperatures were also analysed through SEM-EDS to study the behaviour of the main metals in the range of temperatures. Analysis of copper-rich droplets presented in Fig. 5 shows the agglomeration and channels formed by lead particles throughout the surface of the balls obtained in heat treatments at the three temperatures studied. Tin segregation was seen in the copper-rich droplets surface generated during heat treatments at 1250°C onwards. Tin-rich droplets showed a similar behaviour; lead channels were seen in droplets obtained at the three temperatures, while tin was segregated in the surface from 1150°C onwards (Fig. 5). NMFs obtained after 10 minutes of heat treatment in the range of temperatures were observed to be formed mainly by carbon microfibers and slag, composed of refractories such as silica, alumina and magnesia, which are components of raw PCBs. The carbonaceous/slag phase was produced in all heat treatments, without much variation in its composition.

## 6. Discussion

This study has investigated the utilization of high temperatures to recover materials from waste PCBs with the aim of reducing the environmental pollution caused by landfilling and inappropriate recycling processes of e-waste. Two types of solid fractions were generated after heat treatments at above the melting point of copper temperatures: a metallic phase and a carbonaceous/slag residue. The metallic fraction was composed of red droplets containing high levels of copper, while white droplets had high concentration of tin and lead. Major metals distributed within the droplets were copper, tin and lead. Lead was mainly observed in the metallic phase, with small amounts in NMFs and in decreasing quantities in all solids while increasing temperature. Lead was present predominantly in the metallic phase caused to some extent by its immiscibility with carbon and a weak reaction with silica<sup>66</sup>. Lead amounts were seen to decrease in both types of droplets and also in the NMFs with increasing temperature. A significant proportion of lead was lost in the gaseous fraction in the form of fumes, dusts and mists at these temperatures. Due to the hazardous nature of lead and poor affinity between lead and copper, this aspect could be important as solids contained very small amounts of lead making them less hazardous in nature.

Copper quantities in NMFs were found to decrease with increasing temperatures; metals showed a tendency to remain within the metallic phase in both copper-rich and tin-rich droplets. In white balls, copper amounts increased with temperature. Tin concentration remained stable for all these temperatures, copper tended to form alloys with tin and was retained in the white droplets. These two metals tended to form intermetallic compounds, as indicated by the Cu-Sn binary phase diagram. As a certain amount of copper was present in the white droplets, a little less copper was present in the red droplets. However, it still represented a significant amount. Generally speaking, increasing temperature led to a redistribution of copper in different phases.

Regarding the distribution of base metals within the three solid fractions, iron has a high tendency of forming oxides, and as it is present in the form of oxide initially, it remained as a compound in the NMFs at all temperatures. Nickel tended to remain as metal in the droplets due to its affinity with copper. Zinc was present in amount increasing in NMFs with increasing temperatures, but still tended to stay to a greater extent in the metallic phase.

Precious metals were also found distributed in the solid fractions, but predominantly within the metallic phase due to their high affinity with copper. This behavior did not change with the increment of temperature, so the metallic phase is expected to be an important source of precious metals. The amounts of silver, gold, palladium and platinum, while being quite low, were still higher than their corresponding minerals/ores, so e-waste can be further refined as an important source of materials. These four precious metals tend to be in elemental state as these are noble metals, staying stable at the working temperatures.

Slag-forming metals remained stable in the NMFs at all temperatures, and only traces could be found in the metallic phase. These elements are part of the raw material as refractory oxides ( $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{MgO}$  and others), and at the operating temperatures these elements do not reduce, so were stable as oxides, remaining in the slag/carbonaceous phase. Carbonaceous/slag residue was also found to be an important source of materials, especially carbon. There was negligible affinity between copper and carbon, resulting in the separation of the copper rich metallic phase from the carbonaceous residue. Inert environment prevented the burning and loss of carbon in the gas fraction, reducing the generation of greenhouse gas emissions as well during the recycling process. Carbon microfibers were found to emerge once copper had melted and formed droplets along with other metals. These microfibers were found to be stable at temperatures as high as 1350°C. Lead amounts were decreasing while increasing temperature, which has resulted in a lead-free residue, which could be used as an energy source in several applications.

## 7. Conclusions

Key outcomes obtained in this study upon recycling waste printed circuit boards (PCBs) under inert atmosphere and at temperatures above the melting point of copper are summarized below.

- An effective concentration of metals as a metallic phase, with molten copper acting as a solvent. Key metals present in waste PCBs, i.e. Cu, Sn, Pb showed a tendency to separate out as metallic droplets; other minor metals such as Au, Pd, Pt, Ag, Ni were also found to concentrate in these droplets. On cooling to room temperature, Sn and Pb tended to segregate from the Cu based phase, leading to the formation of highly copper rich metal, which could be directly refined for copper recovery.

- Inert conditions led to the generation of carbon rich/slag residue. Very limited affinity between carbon and copper resulted in the clear separation of metallic phase from the residual carbon. Inert conditions also prevented the re-oxidation of metals and the burning of carbon present in polymers, significantly reducing the generation of greenhouse gas emissions during recycling and avoiding the loss of carbon in the gaseous fraction. Carbons produced during recycling could find application as a valuable carbon source.
- The carbonaceous phase was almost depleted of hazardous Pb which preferred to form solid solutions with the copper rich metallic phase. With increasing temperature metallic phase also became lead-free. This study has shown an appropriate choice of process conditions could lead to an efficient recycling of electronic waste (PCBs) with significant concentration and recovery of metals and minimal generation of secondary waste products.

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